



Charge-transfer surface complex of EDTA-TiO₂ and its effect on photocatalysis under visible light

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ABSTRACT

We investigated the formation of surface complex between TiO₂ and common electron donors (methanol, formic acid, acetic acid, triethanolamine and EDTA) that can absorb visible light through ligand-to-metal charge transfer (LMCT) mechanism. The visible light activity of TiO₂–EDTA complex was outstanding among all tested TiO₂–substrate complexes. The complexation of EDTA on TiO₂ induced a visible light absorption up to 550 nm and exhibited a marked visible light activity for both the reductive conversion of Cr(VI) and the production of H₂. The optimal concentration of EDTA was 100 μM for the reduction of Cr(VI) but much higher (10 mM) for the production of H₂. The EDTA-adsorbed TiO₂ electrode also generated a significant level of photocurrent under visible light irradiation. The LMCT-excited electrons (in TiO₂ conduction band) are subsequently transferred to electron acceptors such as Cr(VI) and protons. The degradation of EDTA on TiO₂ under visible light was significant only in the presence of Cr(VI) that should scavenge electrons with inhibiting the recombination. The surface CT-complex formation between TiO₂ and EDTA was significantly inhibited when the surface of TiO₂ was fluorinated. The isoelectric point of TiO₂ particles suspended in water was gradually shifted to lower pH values with increasing the concentration of EDTA, which supported the formation of surface complex between TiO₂ and EDTA anions. The FT-IR spectra of TiO₂–EDTA complex showed a band centered at 1409 cm⁻¹, which is ascribed to the carboxylate group complexed with TiO₂ surface. The complex IR band was diminished upon fluorinating the surface of TiO₂. The fact that common electron donors like EDTA can form CT-complexes on the surface of TiO₂ and contribute to the visible light activity should be recognized in assessing and understanding the overall photocatalytic activity.

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1. Introduction

Titanium dioxide has been extensively studied because of the great practical value as a photocatalyst for environmental purification and solar energy conversion [1–3]. Its high oxidation power, low price, easy availability, non-toxicity and excellent (photo)chemical stability makes TiO₂-based photocatalytic materials the most practical. However, pure TiO₂ has a bandgap of 3.0–3.2 eV, which is too wide to absorb most portion of solar energy and limits its solar applications. Therefore, the modification of TiO₂ for visible light activity has been tried in many ways such as dye sensitization [4–6] and impurity doping [7–9].

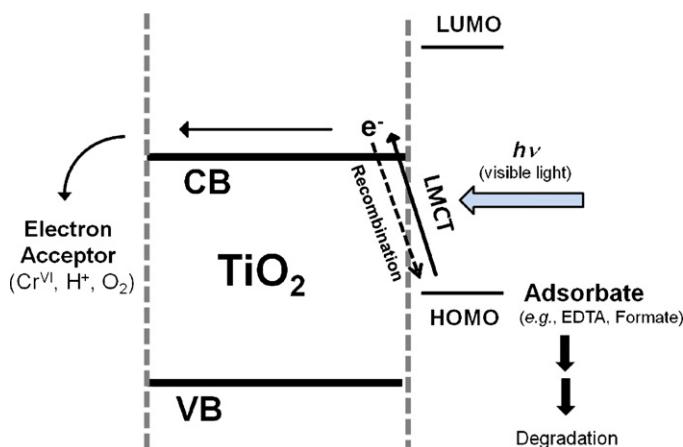
Another way that can modify TiO₂ for visible light absorption is the formation of charge transfer (CT) complex between TiO₂ and surface adsorbate neither of which absorbs visible light [10–14]. This CT-complex-mediated visible light sensitization operates in a mechanism that is different from the common dye sensitization.

In the CT-sensitization, the electron is photoexcited directly from the ground state adsorbate (without involving the excited state of the adsorbate) to semiconductor conduction band (CB) whereas the dye sensitization is mediated through the excited dye state. Many examples of CT-complex formation on TiO₂ surface are known. TiO₂–catechol complex is a classical example of CT-complex. A theoretical calculation study provided evidences that the visible light absorption is attributed to ligand-to-metal charge transfer (LMCT) and the excited state of catechol is not significantly involved in the photoinjection process [15]. TiO₂/8-hydroxyorthoquinoline and TiO₂/1,1-binaphthalene-2,2-diol form surface complexes that absorb visible light and exhibit some activity for hydrogen production under visible light [16,17]. Many organic compounds with phenolic or carboxylic groups (e.g., chlorophenol [18], calixarene [19]) are able to make CT-complexes with the TiO₂ surface for visible light absorption. Recently, a new CT-type visible light photocatalyst was developed by anchoring fullerol on the surface of TiO₂ [20].

Many kinds of organic acids and alcohols are frequently used as a sacrificial electron donor (ED) in semiconductor photocatalytic systems [21–24]. Their primary role is to scavenge valence band

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Scheme 1. Visible light-induced reduction mechanism through the TiO_2 –adsorbate charge transfer complex.

(VB) holes to inhibit the recombination of the charge pairs and EDs by themselves do not absorb any photons in most experimental conditions. In this study, we focus on the possibility of the CT-complex formation of common EDs (methanol, formic acid, acetic acid, triethanolamine and EDTA) on the surface of TiO_2 and demonstrated that some of them do form the CT-complex on TiO_2 with absorbing visible light and exhibit visible light activity for photochemical conversions. **Scheme 1** illustrates the LMCT process in the TiO_2 –adsorbate complex system under visible light irradiation. The visible light irradiation can directly excite an electron from the ground state of the adsorbate to TiO_2 CB when there is a strong electronic coupling between the adsorbate orbitals and Ti d orbitals (a major component of CB). The CB electrons excited through the LMCT mechanism can be transferred to electron acceptors and subsequently initiate a redox reaction, which is clearly distinguished from the bandgap-excited photocatalysis. EDTA (ethylenediaminetetraacetic acid) was particularly active for this LMCT and its visible light activity (for Cr(VI) reduction and H_2 production) through the CT-complex mechanism was investigated with varying experimental parameters systematically. The visible light activity of TiO_2 –EDTA complex is particularly interesting considering the fact that EDTA has been widely used as a common electron donor (or hole scavenger) in many photocatalytic and photoelectrochemical systems employing TiO_2 . This study provides a better understanding on the interfacial electron transfer process occurring on the visible light illuminated TiO_2 surface and its implication for the photocatalytic activity.

2. Experimental

2.1. Chemicals and materials

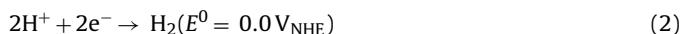
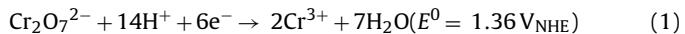
Chemicals used in this study are ethylenediaminetetraacetic acid disodium salt (EDTA, Sigma–Aldrich), methanol (Kanto), sodium acetate (Merck), triethanolamine (TEOA, Aldrich), formic acid (Kanto), sodium fluoride (NaF, Samchun), sodium dichromate dehydrate (Aldrich) as Cr(VI) reagent, diphenylcarbazide (Sigma–Aldrich), acetone (Junsei), chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich), barium sulfate (Acros), potassium bromide (Sigma–Aldrich). All reagents were used as received. Degussa P25 with an average surface area of $50 \pm 15 \text{ m}^2/\text{g}$ was used as a base photocatalyst. Deionized water used was ultrapure ($18 \text{ M}\Omega \text{ cm}$) and prepared by a Barnstead purification system.

Surface fluorination of TiO_2 was carried out by adding 10 mM NaF to an aqueous suspension of TiO_2 (1 g/L). Surface platinization of TiO_2 was done using a photodeposition method as described

elsewhere [25]. Aqueous suspension of TiO_2 (0.5 g/L) was irradiated with a 200 W mercury lamp for 30 min in the presence of 1 M methanol and chloroplatinic acid (H_2PtCl_6). After irradiation, the Pt/ TiO_2 powder was collected by filtration and washed with distilled water. A typical Pt loading was estimated to be ca. 1 wt.% by determining the unused chloroplatinic acid before and after the photodeposition.

2.2. Photocatalytic activity test: Cr(VI) reduction and H_2 production

The visible light activity of the CT-complex of TiO_2 was tested for the following reactions: the reduction of hexavalent chromium ($\text{Cr}(\text{VI}) \rightarrow \text{Cr}(\text{III})$) and the production of H_2 in aqueous suspensions:



TiO_2 powder was dispersed in distilled water (1 g/L) by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. All Cr(VI) reduction reactions were done after 30 min of adsorption equilibration. The pH of the suspension was adjusted with HClO_4 or NaOH standard solution. The light source of photoirradiation was a 450 W Xe arc lamp (Oriel). Light passed through a 10 cm IR water filter and a cutoff filter, then the filtered light was focused onto a 30 mL Pyrex reactor with a quartz window. When the wavelength-dependent photocatalytic activities were investigated, a series of cutoff filters ($\lambda > 420, 455, 495$ and 550 nm) were used. The reactor was stirred magnetically during the reaction. Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45 μm PTFE syringe filter (Millipore). For H_2 production experiments, the aqueous solution containing Pt/ TiO_2 and an ED was deaerated by N_2 sparging for at least 45 min before irradiation and sealed from the ambient air during irradiation. The evolved H_2 gas was sampled from the reactor headspace using a gas-tight syringe. Other experimental conditions were the same as those of Cr(VI) reduction experiments. Duplicate or triplicate experiments were carried out under the identical experimental condition to confirm reproducibility.

2.3. Analysis and characterizations

The concentration of Cr(VI) was determined using the colorimetric method that uses 1,5-diphenylcarbazide reagent [26]. The color change was monitored at 540 nm ($\epsilon = 4 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$) using a UV–visible spectrophotometer (Shimadzu UV-2401). The amount of H_2 production was analyzed using a HP6890A GC equipped with a thermal conductivity detector and a molecular sieve 5A column. The amount of EDTA-adsorbed on TiO_2 was determined by measuring the concentration difference before and after the adsorption of EDTA on suspended TiO_2 particles. Quantification of EDTA was performed using an ion chromatograph (IC) [27]. The IC system was a Dionex DX-120 equipped with a Dionex ion-Pac AS14 (4 mm × 250 mm) column and a conductivity detector. The eluent solution was 3.5 mM Na_2CO_3 /1 mM NaHCO_3 . The zeta-potentials of the suspended TiO_2 particles were measured using an electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka).

The UV–visible absorption spectra of bare TiO_2 and TiO_2 –substrate complex powders were recorded with a UV–visible spectrophotometer equipped with a diffuse reflectance attachment (Shimadzu ISR-2200). The diffuse reflectance UV–visible spectra (DR-UVS) were obtained as follows. A substrate of 10 mM (e.g., EDTA) was added to aqueous TiO_2 suspension (1 g/L) and the pH was adjusted at pH 3. When F- TiO_2 was used to see whether the surface fluorination of TiO_2 influences the TiO_2 –substrate interac-

tion, NaF (10 mM) was added as well. The substrate-adsorbed TiO_2 powder was obtained by filtering the suspension and drying in an oven at 80 °C for overnight. The obtained powder was diluted with barium sulfate ($\text{TiO}_2:\text{BaSO}_4 = 1:1$ by weight) and then measured for DR-UVS.

The formation of TiO_2 -EDTA complex was characterized by FT-IR spectroscopic measurement. EDTA of 1 mM was added to aqueous TiO_2 suspension (1 g/L, pH 3) and the EDTA-adsorbed TiO_2 powder was obtained by the same method used for DR-UVS measurement. The obtained TiO_2 -EDTA powder was diluted in KBr with 1:8 weight ratio and the mixed powder was dried under vacuum condition for overnight. Then a thin pellet was made by pressing the dried powder. The FT-IR spectra of the samples were recorded with the pellet (referenced against a KBr pellet) using a Bomen DA8 FT-IR spectrometer (resolution of 2 cm^{-1}) and 100 interferograms were added for each measurement.

Photocurrent generation was measured with a TiO_2 /FTO electrode immersed in an aqueous solution of substrate such as EDTA. The TiO_2 /FTO electrodes were prepared as described previously [28]. TiO_2 film was coated onto an FTO plate using Carbowax as a binder. Two grams of Carbowax (50 wt.% solution in poly(ethylene glycol)) was mixed with 0.2 g of TiO_2 powder. This TiO_2 /FTO electrode was dried in air for 30 min and heated at 450 °C for 30 min to burn out the binder. The TiO_2 /FTO electrode, a saturated calomel electrode (SCE) and a graphite rod were used as a working (collector), reference, and counter electrode, respectively. The electrolyte used was 10 mM LiClO_4 at pH 3. Nitrogen gas was continuously purged through the suspension. Photocurrent was measured with the application of a potential bias (0.5 V vs. SCE) using a potentiostat (Gamry, Reference 600) connected to a computer.

3. Results and discussion

3.1. Visible light activity and the formation of charge transfer complex

The visible light activities of TiO_2 -substrate complexes were tested for the reductive conversion of Cr(VI) (Eq. (1)) in the aqueous suspension. The removal of Cr(VI) under visible light was compared among many TiO_2 -substrate complexes in Fig. 1a. When EDTA or formate was adsorbed on TiO_2 , 200 μM of Cr(VI) was completely removed within 30 min of visible light irradiation. The visible light activity of TiO_2 adsorbed with methanol and acetate was as low as that of bare TiO_2 and TiO_2 -TEOA exhibited a slight activity. Control experiments (without substrate, TiO_2 or light) confirmed that the removal of Cr(VI) by TiO_2 -EDTA complex cannot be ascribed to the adsorption on TiO_2 , the complex formation with EDTA, nor the direct photochemical reaction with EDTA. In Fig. 1b, the effect of EDTA concentration on the photoreduction of Cr(VI) is shown. The reactivity increased with increasing [EDTA] from 10 to 100 μM but then decreased when [EDTA] further increased to 10 mM. This activity reduction at higher EDTA concentration might be ascribed to the electrostatic repulsion between EDTA and Cr(VI) (chromate) which are both anions. The next paragraph addresses this point. In addition, it should be noted that the visible light activity for Cr(VI) reduction was greatly inhibited when the surface of TiO_2 is fluorinated or platinized as shown in Fig. 1b. The presence of surface fluorides or platinum deposits should hinder the complex formation of EDTA with the surface titanol group. The surface fluorination of TiO_2 substitutes the surface hydroxyl group ($>\text{Ti}-\text{OH}$) by the surface fluoride group ($>\text{Ti}-\text{F}$) and inhibits the surface complex formation and adsorption of substrates [20,29,30]. In addition, the observation that the surface platinization reduced the visible light activity rules out the possibility that the observed photoreduction of Cr(VI) on TiO_2 -EDTA might be caused by the presence of UV light

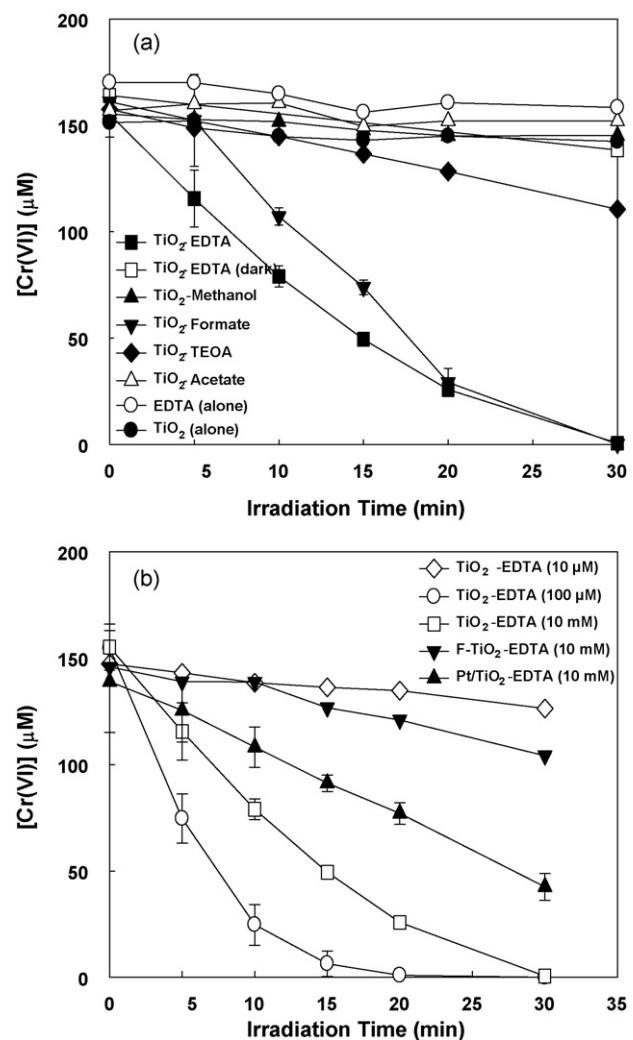


Fig. 1. (a) Cr(VI) reduction in aqueous suspension of TiO_2 with various substrates under visible light. The experimental conditions were $[\text{TiO}_2] = 1 \text{ g/L}$, $\text{pH} = 3$, $\lambda > 420 \text{ nm}$, $[\text{Cr(VI)}]_i = 200 \mu\text{M}$, $[\text{substrate}] = 10 \text{ mM}$. (b) Effects of EDTA concentration and the surface modification of TiO_2 (fluorination and platinization) on the reduction of Cr(VI) under the same experimental condition as (a).

that could leak through the cutoff filter. Since the UV-induced photocatalytic activity of TiO_2 should be enhanced when the surface is platinized [31,32], the UV light leaking through the filter, if any, should have increased the conversion rate of Cr(VI) with Pt/ TiO_2 , contrary to the observation.

Fig. 2 shows the pH-dependent variation of the zeta-potential of suspended TiO_2 particles in the presence of EDTA. The adsorption of EDTA anions on TiO_2 shifted the zeta-potential to the negative direction, which confirms the surface complex formation between EDTA and TiO_2 . The higher [EDTA], the greater the change of zeta-potential. As a result, the point of zero zeta-potential (PZP) (or an isolectric point) is gradually moved to lower pH value with increasing [EDTA]. At pH 3, the zeta-potential of TiO_2 is positive with $[\text{EDTA}] \leq 1 \text{ mM}$ whereas it is negative with $[\text{EDTA}] = 10 \text{ mM}$. Therefore, the adsorption of chromate anions on TiO_2 -EDTA should not be favorable at $[\text{EDTA}] = 10 \text{ mM}$ where the surface charge is negative. This explains why the Cr(VI)-reduction activity decreased when the EDTA concentration increased from 100 μM to 10 mM in Fig. 1b.

The fact that some TiO_2 -substrate complexes exhibit the visible light activity indicates that the complexes should absorb visible light. Fig. 3 shows that DR-UVS of the substrate-adsorbed TiO_2

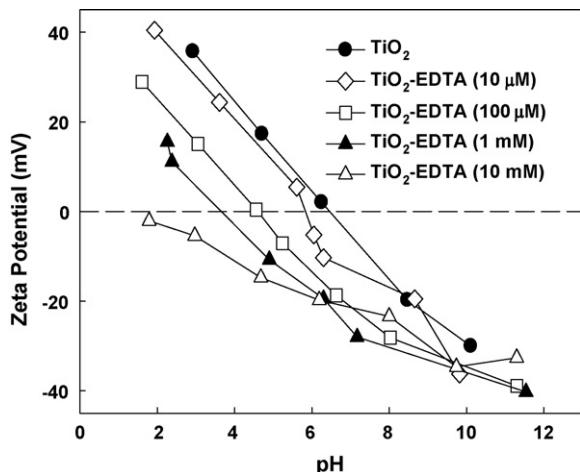


Fig. 2. pH-dependent zeta-potential of the suspended TiO_2 particles in the presence of different concentration of EDTA ($[\text{TiO}_2] = 2 \text{ mg/L}$, $[\text{NaNO}_3] = 1 \text{ mM}$).

powders do have visible absorption above 400 nm although neither TiO_2 nor the tested substrate (methanol, formic acid, acetic acid, TEOA and EDTA) alone absorbs visible light. The visible light absorption was observed for not only $\text{TiO}_2\text{-EDTA}$ and $\text{TiO}_2\text{-formate}$ that exhibited significant visible light activity but also other surface complexes of which activity was insignificant. The $\text{TiO}_2\text{-methanol}$ complex showed a marked absorption of visible light despite the lack of visible light activity. On the other hand, when the surface of TiO_2 was fluorinated, the visible light absorption was markedly reduced, which is consistent with the quenching of the visible light activity on F-TiO_2 (see Fig. 1b). This implies that the origin of the visible light activity of TiO_2 in the presence of EDTA should be ascribed to the formation of CT surface complexes that absorb visible light.

The surface complex formation was investigated by FT-IR spectroscopic measurement for $\text{TiO}_2\text{-EDTA}$. In Fig. 4, there are one broad band at 1409 cm^{-1} and another at 1628 cm^{-1} , which is consistent with a previous FT-IR measurement of EDTA-adsorbed on TiO_2 [33]. The latter band (1628 cm^{-1}) that is observed for both bare TiO_2 and $\text{TiO}_2\text{-EDTA}$ is ascribed to the surface adsorbed water and hydroxyl group [34,35]. The former band (1409 cm^{-1}) that is observed only in the presence of EDTA corresponds to the symmetric stretching of the carboxylate group. When the surface of TiO_2 is fluorinated, the intensity of this band is considerably reduced, which is also consistent with the reduced visible light activity of F-TiO_2 . This

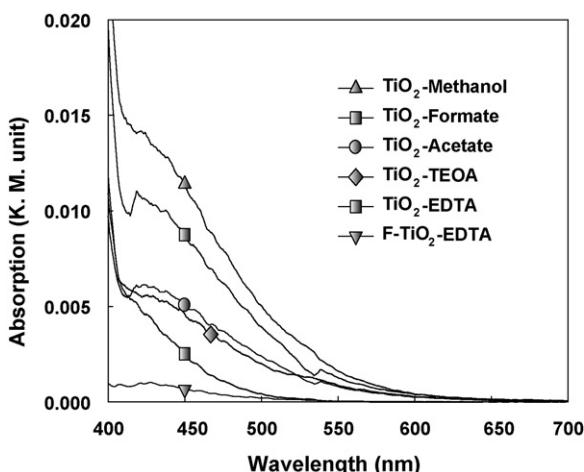


Fig. 3. Diffuse reflectance UV-visible spectra of TiO_2 -adsorbate powders with the reference taken as bare TiO_2 powder.

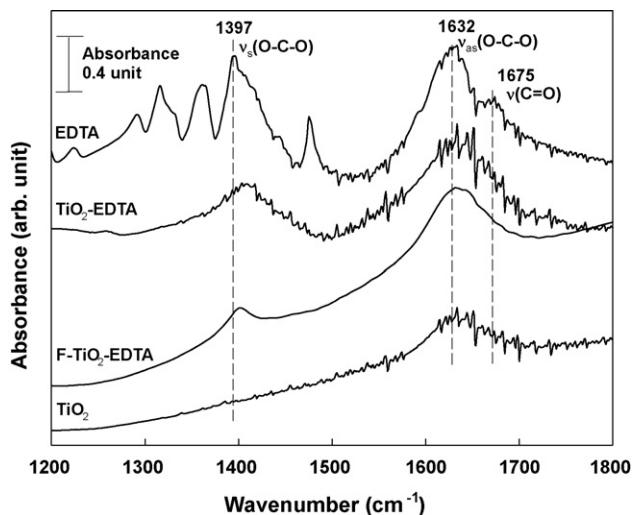
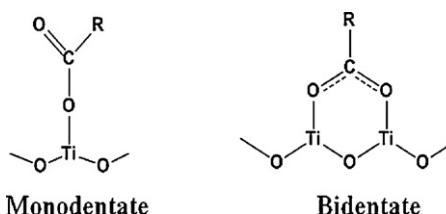


Fig. 4. FT-IR spectra of bare TiO_2 , pure EDTA, $\text{TiO}_2\text{-EDTA}$ and $\text{F-TiO}_2\text{-EDTA}$ powder pellet samples (diluted with KBr, referenced against KBr).

confirms that the presence of surface fluorides inhibits the formation of the surface complex. The possible bonding modes for $\text{TiO}_2\text{-EDTA}$ complex are mono- and bidentate through the carboxylate ligand, as illustrated in Scheme 2. To clarify the bonding mode, the FT-IR spectrum ($1200\text{--}1800 \text{ cm}^{-1}$ region) of free EDTA (disodium salt form) is also compared in Fig. 4. The major IR bands of carboxylic group of free EDTA are as follows: 1675 cm^{-1} for the C=O stretching mode ($\mu_{\text{C=O}}$); 1632 cm^{-1} for the antisymmetric stretching mode (μ_{as}) of (O-C-O) [33]. If the $\text{TiO}_2\text{-EDTA}$ complex has the monodentate mode, $\mu_{\text{C=O}}$ band should appear. The fact that this band ($\mu_{\text{C=O}}$) is absent for $\text{TiO}_2\text{-EDTA}$ indicates that the bidentate binding mode is favored. The μ_s band is clearly observed with $\text{TiO}_2\text{-EDTA}$ and its band position is slightly shifted to a higher wavenumber ($1397 \rightarrow 1409 \text{ cm}^{-1}$), which indicates that the carboxylate group is indeed bound to Ti centers as Scheme 2 illustrates.

To investigate the wavelength-dependence of the visible light activity of the $\text{TiO}_2\text{-EDTA}$ complex, the photoreduction of Cr(VI) was carried out under different irradiation wavelengths which were controlled by changing the long-pass cutoff filter. Fig. 5a compares the absorption spectrum (DR-UVS) of the $\text{TiO}_2\text{-EDTA}$ complex with the transmittance profiles of the cutoff filters used for irradiation. Because the visible light absorption profile of the $\text{TiO}_2\text{-EDTA}$ complex gradually decreases from 400 to 550 nm, fewer photons should be absorbed by the surface complex at longer wavelengths. The wavelength-dependent visible light activities for Cr(VI) conversion are compared in Fig. 5b. The activity is gradually getting lower at longer wavelengths and negligible at $\lambda > 550 \text{ nm}$ in which the visible absorption vanishes. The activity dependence on the irradiation wavelengths clearly indicates that the photoreduction of Cr(VI) is induced by the LMCT excitation of the $\text{TiO}_2\text{-EDTA}$ complex as Scheme 1 describes.



Scheme 2. The possible coordination structures of EDTA-adsorbed on TiO_2 surface.

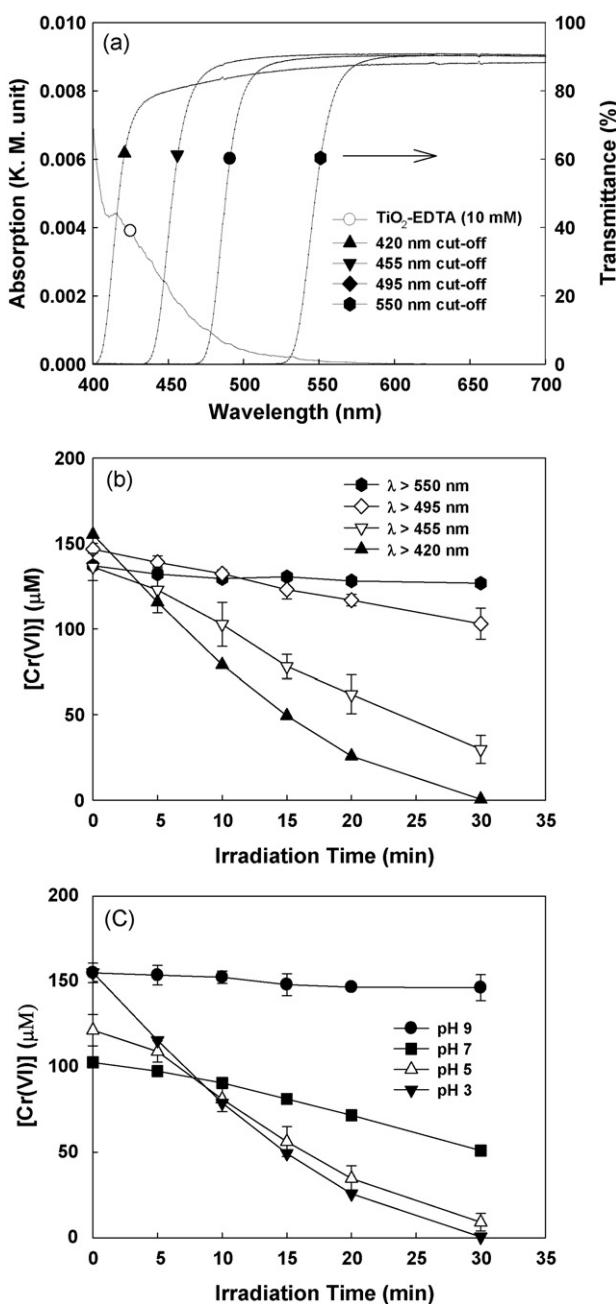


Fig. 5. (a) Diffuse reflectance UV-visible spectra of TiO_2 -adsorbate powders compared with the transmittance profiles of the cutoff filters that were used in controlling the irradiation wavelengths. (b) The irradiation wavelength-dependent and (c) pH-dependent photoreduction of Cr(VI) with TiO_2 -EDTA under visible light. Other experimental conditions were the same as those of Fig. 1a.

The visible light activity of the TiO_2 -EDTA is also strongly dependent on pH as Fig. 5c shows. The activity for Cr(VI) conversion was significant only at acidic condition, markedly reduced with increasing pH, and negligible at pH 9. This should be mainly ascribed to the pH-dependent surface charge of TiO_2 . Because the surface charge of TiO_2 is predominantly negative at basic condition (see Fig. 2), the surface interaction with EDTA and chromate anions should be inhibited by the electrostatic repulsion. Therefore, the TiO_2 -EDTA surface complexes that absorb visible light cannot be formed at alkaline pH and no visible light activity should be observed.

The electron injection onto TiO_2 CB through LMCT was also monitored by measuring the photocurrent with the substrate-adsorbed TiO_2 /FTO electrodes under visible light. The level of the steady-

Table 1

Visible light-induced photocurrent generation (ΔI_{ph}) with the TiO_2 electrode in the presence of various substrates.

| | $\Delta I_{\text{ph}} (\mu\text{A})^{\text{a}}$ |
|--------------|---|
| EDTA | 4.21 (± 0.54) |
| Formate | 1.76 (± 0.21) |
| Acetate | 0.45 (± 0.05) |
| TEOA | 0.40 (± 0.07) |
| Methanol | 0.34 (± 0.20) |
| No substrate | 0.48 (± 0.05) |

^a ΔI_{ph} was determined from the difference before and after 500 s of light irradiation.

state photocurrents is compared among the tested substrates in Table 1. The photocurrent results are consistent with the photoactivity for Cr(VI) conversion. Only EDTA and formate that showed a significant visible light activity generated the level of photocurrent which is significantly different from that obtained with the bare TiO_2 electrode. Although the methanol- TiO_2 complex absorbs a significant fraction of visible light, its ability to generate the photocurrent under visible light is as negligible as the activity for Cr(VI) conversion. It seems that the electron excited through LMCT in the TiO_2 -methanol system rapidly recombines with the oxidized methanol as illustrated in Scheme 1.

The LMCT excitation of the adsorbed EDTA should oxidize EDTA itself with initiating its degradation. The visible light-induced degradation of EDTA on TiO_2 was monitored and shown in Fig. 6. The control experiment shows that EDTA cannot be degraded by chromate in the dark condition although chromate is a strong oxidant. The degradation of EDTA should be a photochemical process. The removal of EDTA in the suspension of TiO_2 proceeded as fast as the conversion of Cr(VI) (compare Fig. 1b vs. Fig. 6) but was insignificant in the absence of Cr(VI). This can be explained in terms of the role of chromate as an electron acceptor. As Scheme 1 shows, the electron injected into TiO_2 CB either transfers to an electron acceptor or recombines with the oxidized EDTA. In the absence of the electron scavenging Cr(VI), the injected electrons mostly recombine with making a null cycle and the degradation of EDTA is inhibited. The overall activity of the adsorbate- TiO_2 complex in inducing the visible light-sensitized reactions should be limited by the recombination process (or back electron transfer) which should be influenced by the presence and kind of electron acceptors (e.g., Cr(VI) in this case).

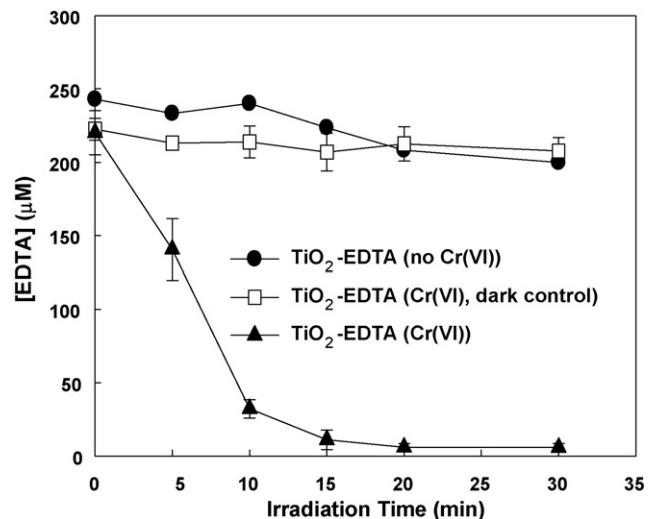


Fig. 6. The time profiles of EDTA degradation in the suspension of TiO_2 with or without Cr(VI) under visible light. $[\text{EDTA}]_i = 300 \mu\text{M}$. Other experimental conditions were the same as those of Fig. 1a.

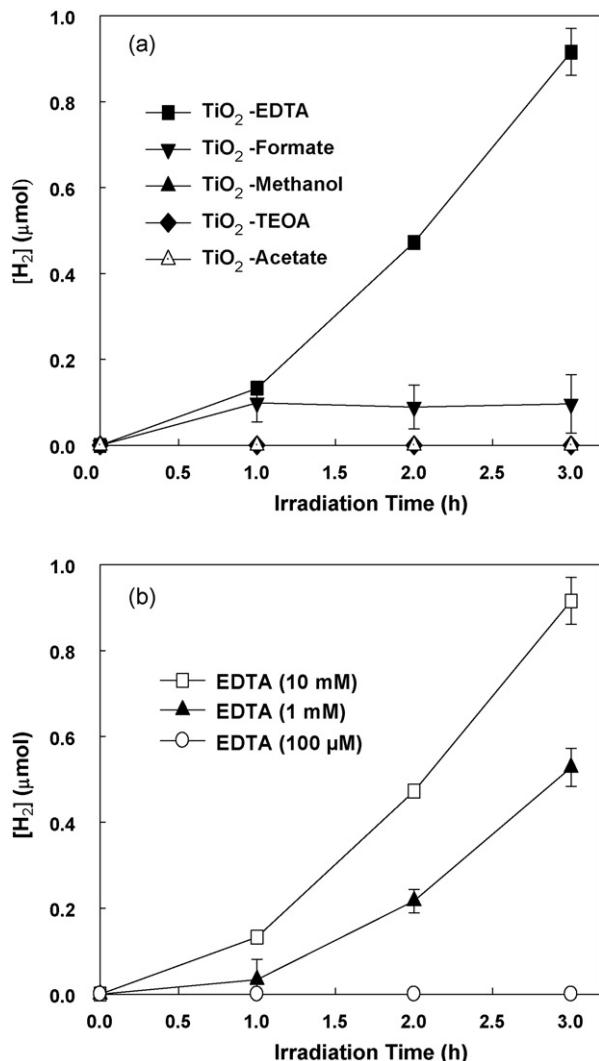


Fig. 7. Time-dependent profiles of hydrogen generation in the visible light-irradiated suspension of TiO_2 (platinized) with changing (a) the kind of electron donors and (b) [EDTA]. Other experimental conditions were the same as those of Fig. 1a.

3.2. Visible light activity of the charge transfer complex for the production of H_2

In the absence of external electron acceptors, water and proton should play the role with producing H_2 (Eq. (2)). The visible light activity of TiO_2 -EDTA complex was also tested for the production of hydrogen. In this case, the surface of TiO_2 was photodeposited with Pt before adsorbing EDTA. Fig. 7a compares the activity of TiO_2 -EDTA with other TiO_2 -substrate complexes. As in the case of Cr(VI) conversion, only TiO_2 -EDTA and TiO_2 -formate complexes exhibited the visible light activity. However, the TiO_2 -formate complex was active only for the initial 1 h unlike the case of Cr(VI) while the TiO_2 -EDTA complex continuously generated H_2 during 3 h of irradiation. Since protons are much weaker electron acceptors than Cr(VI), the charge recombination (see Scheme 1) in the TiO_2 -EDTA- H^+ system should be more favored than that in the TiO_2 -EDTA-Cr(VI) system. The fact that the TiO_2 -EDTA complex is far more active than the TiO_2 -formate complex probably implies that the charge recombination is slower in the TiO_2 -EDTA complex. This is supported by the fact that the TiO_2 -EDTA electrode generated higher photocurrent than the TiO_2 -formate electrode despite

the higher visible light absorption by the latter (see Table 1 and Fig. 3).

The dependence of H_2 production activity on [EDTA] is also quite different from the case of Cr(VI) conversion. In the TiO_2 -EDTA-Cr(VI) system both EDTA and chromate are anions competing for surface sites. Therefore, the conversion of Cr(VI) was optimized at [EDTA] = 100 μM . On the other hand, the production of H_2 was completely negligible at [EDTA] = 100 μM and increased with [EDTA] up to 10 mM (compare Figs. 1b and 7b). The markedly different dependences on [EDTA] between the TiO_2 -EDTA- H^+ and TiO_2 -EDTA-Cr(VI) systems indicates that the reduction of protons is much less favored than that of Cr(VI) probably because of the faster recombination in the former (see Scheme 1). The optimal surface concentration of CT-complexes for the maximal sensitization efficiency seems to depend on the kind of photoconversion reactions.

4. Conclusions

This study demonstrated that common electron donors (i.e., EDTA and formate) that are widely used in the photocatalytic and photoelectrochemical systems can form the visible light-absorbing CT-complexes on the surface of TiO_2 although the electron donor itself cannot absorb any visible light. The TiO_2 -EDTA system was selected as a model case of the CT-complex and its visible light activity was investigated as a function of various experimental parameters. The visible light absorption of the TiO_2 -EDTA complex (extended up to 550 nm) is initiated through LMCT which excites an electron directly from the ground state of EDTA to TiO_2 CB. The electrons excited to CB can be transferred at the interface when suitable electron acceptors are present. In this study, the photoreduction of Cr(VI) to Cr(III) and H^+ to H_2 was employed as test reactions that demonstrated the visible light activity. The formation of the visible light-absorbing TiO_2 -EDTA complex was inhibited when the surface of TiO_2 was fluorinated, which was supported by the reduced activity for Cr(VI) conversion, DR-UVS and FT-IR spectra. Considering that EDTA has been commonly used as an electron donor in TiO_2 photocatalysis, the fact that TiO_2 -EDTA complex can absorb visible light and may induce photocatalytic reactions should be taken into account in understanding the photocatalytic activity and mechanism. However, it should be mentioned that this study did not intend to use EDTA as a photosensitizer for developing visible light photocatalyst. TiO_2 -EDTA cannot be employed as an efficient and stable visible light photocatalyst since the visible light absorption is weak and EDTA is degraded as a result of the CT-reaction.

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